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DIFFERENTIAL THERMAL ANALYSIS

METHODS AND TECHNIQUES

By

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INTRODUCTION

All reactions are accompanied by energy changes which generally manifest themselves as heat energy. Some produce heat and are called exothermic; some require heat for the reaction to proceed and are called endothermic. The presence of such heat effects during the heating of clays was first shown potentiometrically in 1887 by LeChetalier[1]. Nothing else was done along these lines for a long time. This phenomenon was again reported on in 1913 by Wallach[2] and in 1923 by Houldsworth and Cobb[3]. It did not, however, receive extensive popular attention until after Norton's[4] work which was reported in the Journal of the American Ceramic Society in 1939. The method of Differential Thermal Analysis, as it is known, has reached the prominence of other techniques such as x-ray diffraction, microscopes, etc. as a helpful research and control tool. Its importance is increasing because of the development of equipment refinements, and because of the potential value of the data with the growth of the knowledge of crystal chemistry and thermodynamics of non-metallics.

The adoption of the indicated name for the technique is based on the method of measurement which determines the difference in temperature between the sample and the reference material or furnace by means of a differential thermocouple. A differential thermocouple is preferred to simply measuring the individual true temperatures and taking the difference because of the increase of sensitivity derived by a tremendous expansion of the temperature scale which is physically possible by measuring the difference directly. Alpha-alumina is most commonly used as a reference material because of its lack of

heat effects throughout the temperature range of interest, and because of its similarity to most ceramic materials in thermodynamic properties. However, it is possible to use other materials.

GENERAL EXPERIMENTAL TECHNIQUES

A Differential Thermal Analyzer is composed of three major components: a sample holder, a controlled source of heat, and a device for the measurement of the heats of reaction. Fundamentally only a few basic ideas exist although practically no two units are exactly alike in detail because they are generally assembled individually. The actual design employed, in addition to personal preferences, is primarily controlled by economic factors and the ultimate purpose of the data.

Sample Holder

The usual type of sample holder, as shown in Figure 1, is a rectangular parallelepiped block with two comparatively large holes, one for the sample and one for the reference material. These have small holes drilled into their sides through which the differential thermocouple junction beads are inserted, although it is possible to do it in other ways. The junction beads can be inserted through the top in instances where the sample may melt and also in cases where the sample may react with the ceramic insulator used to bring in the thermocouple junctions through the side holes. Another hole in the side center holds the bead for the furnace or block temperature thermocouple.

The size of the holes is a design feature based on a compromise between the principles that the sample should be as small as possible in order to minimize the temperature gradients through the sample powders and, on the other hand, as large as possible in order to increase the magnitude of heat effects which thus would become easier to measure.

Another design question is the determination of the overall volume of

the block relative to the volume of the holes. One proposed theory is that a certain minimum mass of the block is desirable to act as a heat stabilizer and thus eliminate temperature fluctuations due to fluctuations of thermal radiations brought about by on-off temperature controls frequently used and to act as an insulator in preventing heat flow between the two materials. Another theory, conversely, is that the mass of the block should be as small as possible in order to eliminate any tendency for minimization of sharpness of thermal effects because of absorption of heat by the block - a heat capacity effect. An extreme example of this idea is the use of two separate thin-walled platinum crucibles for holding the alumina and sample, as reported by Gruver(5).

Errors are introduced if the differential thermocouple beads are not at the symmetrical center of the cavities, as pointed out mathematically by Smyth(6). An unusual method to eliminate the difficulty of centering of couples, as reported by Herold and Planje(7), consists of building the sample and reference holders as huge thermocouple junction cups. A disadvantage of the method is that errors in sample temperature measurement result, primarily in cases when the sample shrinks from the walls of the cup.

In cases where it is necessary to test large numbers of samples, blocks have been designed to heat more than one sample simultaneously(8). In such cases either one common reference hole or a separate reference hole for each sample hole are used depending on the method of temperature recording.

The material of the block is governed by cost, test temperatures to be attained and the degree of inertness relative to both the sample and reference material. The usual material is relatively inexpensive nickel which can be used indefinitely in runs up to 1000°C. In cases where higher temperatures are desirable platinum or platinum-rhodium are commonly used. Some tests, especially by the English(9), have been made using a ceramic block. In this case advantages in comparison with metal blocks are a lower heat content and a lower

thermal conductivity. In fact, any material can be used provided it is stable and does not react with the test materials. Runs were made in this laboratory using graphite blocks for materials that showed some reactivity with the metals.

Controlled Heat Sources

The furnaces are usually of the tubular type, wound with electrical resistance wire of nichrome - for temperatures up to approximately 1000°C., with kanthal - up to approximately 1350°C., and with platinum-rhodium - up to approximately 1500°C. Wherever possible, the nichrome is preferred because of lower cost, ruggedness, and maintenance of practically a constant resistance with increase of temperature. Platinum or its alloys are necessary for the higher temperatures but greater precautions must be taken because of the variable electrical resistance of the platinum with temperature, and especially because of its low resistance at low temperatures. Also, for the higher temperatures it presumably would be possible to design a furnace heated by Globar elements. The heat control, in this case, would have to be designed to take care of the change of resistance of the Globars with time.

The internal dimensions of the furnace are usually just large enough to hold the sample block and its support. The set-up involves an arrangement whereby the furnace can be lowered vertically or pulled horizontally over the support which should be easily accessible for the preparation of the run. The horizontal furnace set-up as explained by Speil, Berkelhamer, Pask and Davies[10] is commonly used.

Accurate temperature control is essential because all of the experimental factors have to be constant in order to obtain repetitive results. The heating rate is critical only in the sense that it has to be the same from run to run in a given laboratory. This can be attained by following a certain power-input pattern. Where program controllers are available, a heating rate of so many degrees or so many millivolts per minute is maintained. Rates of 6°C./min. to

25°C./min. have been used. In maintaining a constant rate on the basis of mv./hr. the temperature curve is curvilinear on a °C./time basis because of the variability of mv./°C. with change in temperature. A straight line heating curve is preferred for it is easier to report, although actually this is not a requirement for good results providing whatever heating pattern is used is always repetitive.

Recording of Differential Temperature

The most significant variations between assemblies in different laboratories are in the method of recording the differential temperatures. It lends itself to variation of ideas because of the difficulties encountered in reliably detecting the small differences in temperature in small test samples. From both an apparatus and cost viewpoint the simplest methods are manual. Data can be obtained with a suspension type galvanometer and recorded versus time by an observer throughout a test. If it were calibrated, the deflections would correspond to mv. or temperature. Similarly, the same readings can be made directly in millivolts with a sensitive research potentiometer, such as Leads & Northrup's Type K.

Most methods employed are automatic in order to obtain a direct record and to avoid the tediousness of taking numerous readings and perhaps the possibility of missing essential readings during rapid changes in temperature or very small thermal effects. The least expensive of these methods consists of an arrangement wherein the reflection of a fixed light source from the mirror of a suspension type galvanometer is directed through a slit into an otherwise light-tight box containing a sheet of photographic paper mounted on a roll operated by a clock mechanism. The disadvantages of the method are the inability to observe the development of the curve during the test, and the necessity of photographic development.

The most desirable set-up uses a recording millivoltmeter or potentiometer

which produces an observable record directly and also indicates actual instead of relative temperatures. The main difficulty is in obtaining instruments with sufficient sensitivity to measure the small temperature differences. A number of special voltage amplifying circuits have been developed, which have been used both as a separate unit and as an integral part of the potentiometer. One experimental scheme has been to use potentiometers with the smallest millivolt range available and then designing a suitable sample holder that will result in the development of sufficiently large heat effects to be recordable. Such a potentiometer produces a curve of temperature difference versus time. The time scale is then converted to furnace temperature. A refinement of this arrangement is the use of X-Y potentiometer recorders which produce a direct record of difference against furnace or block temperature making it easier to compare curves. The use of the X-Y instrument also enables the easy obtainance of curves for temperature difference vs. sample temperature.

Special Units

All of the above arrangements are descriptive of experimental systems that are not movable and constitute a permanent laboratory installation. However, in field work it is sometimes highly desirable to obtain information on mineral constitution at the moment. In such instances a unit that could easily be taken into the field would be highly desirable. Such a unit has been developed by the U.S.G.S. and described by Hendricks, Goldrich, and Nelson[11]. The basic principles are the same although the sensitivity of the instrument is inadequate for exacting research work.

Other Special Units

Special modifications are possible. The set-ups described are operated under normal atmospheric conditions. It is possible to build apparati wherein the atmosphere can be controlled. Stone[12] has constructed a unit in which water vapor and gas pressures could be varied. Runs have been made in this

laboratory in a dynamic helium atmosphere. Runs can be made in vacuum by construction of a suitable unit.

At present the top temperature for D.T.A. is limited by the thermocouple, most commonly platinum-rhodium. Some combinations of tungsten-molybdenum may be used for higher temperatures in controlled atmospheres. Other methods for differential temperature measurement may be conceived above this range.

DEVELOPMENT OF UNIVERSITY OF CALIFORNIA EQUIPMENT

The University of California equipment was designed for thermal reaction research as well as for purposes of identification of minerals, such as clays and talcs. The overall set-up has been generally described by Pask(13). It was desired to have a range of approximately 1500°C. and a recording system of the potentiometer type which produces a permanent record that could be observed during its development. Because of this temperature requirement platinum or one of its alloys was necessarily the block material. Another advantage of platinum is its relative inertness and thus the possibility of cleaning it in case of fusion of the sample.

The narrowest full scale span available in a potentiometer at the time, without the use of auxiliary amplifying units, was 0.5 millivolts which with a center zero provided a range of -0.25 to 0 to +0.25 millivolts. Although this was an extremely sensitive recording-type of potentiometer, it was still insufficient to pick up satisfactorily the small heat effects using a platinum-rhodium differential thermocouple and the usual block design. Thus, one of the early tasks was the design of a test block.

Other difficulties arose, as well, in regard to effects of fluctuations of heating rates and a.c. pickups of various sorts, especially at temperatures above 1100°C. A discussion and presentation of development results follows which may serve as an aid to those contemplating acquirement and use of such equipment.

Block Design

The volume of the holes and the ratio of the overall bulk volume of the block to the volume of the sample holes were varied. During this development stage, nickel was used for the blocks and the runs were necessarily terminated at about 1000°C. Differential thermal analyses curves of a ball clay and two talcs, were obtained for each specific combination tested. Talc A contains a small amount of chlorite and dolomite as impurities. Talc B contains amphibole, dolomite, and calcite as impurities.

Figure 2 shows the D.T.A. curves for the ball clay as obtained in nickel blocks with varying combinations of hole diameters, ¼" 3/8" and ½" and of ratios of bulk block volume to volume of sample holes, 2.7, 5.8 and 10.6. Similar curves are shown for Talc A in Figure 3 and for Talc B in Figure 4. Larger hole diameters were not possible because of geometrical limitations of the furnace design. The curves as reproduced represent differential temperature versus the block temperature.

As would be expected it is seen, that for a given heating rate, the sizes of the peaks increase. Because the thermal effects always start at about the same temperature, the peak temperature for a given reaction, generally measured as furnace temperature, shifts to higher values since a longer time is necessary for the completion of reaction. The degree of shift, however, is not constant and is dependent upon the test material because it is controlled by the rate of reaction. Thus, if it is desirable to increase the sensitivity to show up reactions accompanied by small heat effects, the size of the sample can be increased. This procedure works satisfactorily as long as the reactions in question are fairly well isolated from each other. If the reactions occur within a narrow temperature range, however, such a procedure will lessen the resolving power because the peaks will begin to overlap on account of the fact that a given peak always starts at about the same temperature. Thus, if a

number of reactions occur close to each other, the size of the sample should be reduced in order to get maximum resolving power. This point is excellently illustrated by curves for Talc B (Figure 4). Maximum number of reactions are shown by blocks with $\frac{1}{4}$" diameter sample holes. As the samples get larger, the peaks begin to merge and lose identity.

Oxidation reactions, such as oxidation of the carbonaceous material in the ball clay as shown by the exothermic activity below about 900°C in Figure 2, are more sensitive to sample size variations than decompositions. The peak of the exothermic activity shifts to higher temperatures with increase of size of hole. This type of shift could interfere with the balance of the curve because the actual D.T.A. curve is a resultant of all heat effects. Thus, tests have been frequently run with helium gas purging the furnace in which case the true reactions of the clay are revealed without the exothermic interference due to oxidation of carbon.

A change in ratios of the bulk block volume to the volume of the sample holes had correspondingly minor affects. There was, in general, a slight but not significant increase in size of thermal peaks and a shift with increasing ratios. This can be observed by a comparison of the D.T.A. curves.

An interchange of platinum for nickel as block materials caused slight but not significant increases in size of peak. Graphite was also tried as a block material without any significant changes in the D.T.A. curve. Thus, material selection should be based essentially on factors of cost and possible reactivities with sample.

In the course of the experimental development several tests were run with separate unconnected sample holders. There was no significant improvement in resolving power or sensitivity. Thus, because of the greater manipulation difficulties, this approach was abandoned in favor of the single block.

On basis of the above information the final design for general use was

one that had sample and reference volume holes as small as possible for maximum resolving power but large enough to obtain sufficient thermal activity to develop a satisfactory size peak with the available differential temperature recording arrangement. Furthermore, in the interests of economy, because platinum was being used, the ratio of the bulk volume to the volume of the holes was made as small as possible with the retainment of ruggedness and mechanical stability of the block. The dimensions of the block now being used are shown in Figure 1.

Heating Rates

Heating rates of 5.6, 9.0, and 12.0 mv./hour, using a platinum-10% rhodium thermocouple were employed. These are not exactly straight line curves for temperature vs. time (mv./°C. is not constant for a thermocouple) but were used because of the nature of the available temperature controlling equipment. Any heating rate, however, providing it does not reverse its slope is satisfactory as long as it is definitely repetitive. The above heating rates correspond approximately to an average of 9°C./min, 15°C./min, and 20°C./min.

Figures 2 and 4 for Ball Clay and Talc B show the effect of varying the heating rate. With increasing rates the endothermic effects shift to higher temperatures. The oxidation temperature range of the carbon in the ball clay is also shifted to higher temperatures. Thus, the best heating rate was 5.6 mv./hr. especially with blocks having 3/8" diameter sample holes. If the heating rate becomes too slow, then sensitivity is lost because of the greater probability for heat dissipation to the system. The critical limit was not determined. In going up to 1500°C., however, this rate was impractical because of the long time involved for a test run. The final selected heating rate for general routine runs was a compromise of these factors and consideration of equipment manipulation at 9 mv./hr. or approximately 15°C./min.

In operation it was found that slight deviations in the straight line

heating curve, especially with changes in direction of slope, resulted in similar deviations in the differential temperature curve that could easily be mistaken for a heat effect. The design of the apparatus thus had as ultimate goal of a constant or a uniformly constantly changing heating rate. A clock motor was first attached to the Variac to provide a constantly progressive increase of part of the voltage which was controlled by an on-off type of potentiometer controller, the remaining voltage being continuously fed to the furnace.

Although this heating arrangement worked well the on-off feature was still troublesome, especially above temperatures of about 1100°C. A circuit is now being used wherein the Variac is controlled by a motor drive which in turn is controlled by the demands of the programmed heating rate.

Other Factors

At these higher temperatures the system becomes extremely sensitive to a.c. strays. Both legs of the thermocouples are grounded through condensers to bypass the a.c. current to ground. The sample block and the furnace are also grounded, and all the thermocouple leads are shielded. Other difficulties arose, such as the increased electrical conductivity of the furnace lining upon which the platinum resistance wire is wound. Steps were taken to prevent contact of the sample holder with the furnace tube to avoid a.c. leakage from the heating circuit to the differential thermocouple circuit. These difficulties will become less troublesome with the development of better filter circuits on the part of the potentiometer manufacturers.

The differential thermocouple, as previously mentioned, is a platinum-rhodium one, and the size of the wires used is 8 mils. The fine wire size reduces heat transfer along its own length, and permits better imbedding within the sample and the reference material. Furthermore, its cost is small and permits frequent replacement because of contamination and fusion of sample

without creating an economic problem.

The "zero" line for a run may shift from the true zero of the instrument because of difference in heat capacities between the sample and the reference alumina. However, sometimes the D.T.A. curves "drift" continuously either in one or the other direction. This effect can be caused by non-central positioning of the thermocouple junction beads within the holes of the sample block or the block itself within the furnace core. Such a drift means, essentially, that one side of the differential thermocouple is getting hotter because of uneven heating.

THERMAL REACTIONS

Endothermic and exothermic reactions under repetitive experimental conditions occur at fixed temperatures. Such reactions then become fingerprints by which materials can be identified and reactions between materials can be studied. On a rising temperature basis, endothermic heat effects can be caused by the following reactions:- vaporization, decomposition, inversion, reduction, and fusion. The exothermic ones are due to oxidation and crystallization. On cooling, the heat effects that would repeat themselves would be reversed.

The physical shape of the peak and the temperature of reaction is determined by the position of the temperature thermocouple. It can be located either in the furnace or block which in most instances is similar to furnace temperature, or in the unknown sample, or in the reference sample which is usually alumina. In the first case the true reaction temperature corresponds to the initial departure from the straight line portion; in the second, the reaction temperature corresponds to the peak of the curve; and in the latter, the reaction temperature corresponds to neither and is in-between the two which, thus, is the poorest arrangement.

In most test units the furnace temperature is measured separately and thus

the problem of transposing this temperature and the differential to the same graph exists. With this set-up because of lags and accelerations that may occur in the test sample relative to the furnace temperature, it is experimentally convenient to use the block temperature as the test temperature. With the development of the X-Y recorder and its use it will be possible to record the differential temperature directly against the temperature of the sample, which might have some advantages.

Factors Affecting Shape of Reaction Peaks

A number of papers have appeared showing that the area of the peak inscribed by the reference line and the differential temperature line is proportional to the amount of a certain material by weight. The amount of material along the shortest path from the thermocouple bead to the boundary of the sample is apparently the amount in question. In this case it would be the horizontal direction, that is, perpendicular to the axis of the hole. Talc A was packed in the sample hole in amounts of 0.5, 0.8, and 1.0 grams. With the latter two weights of material the D.T.A. curves were practically identical, indicating that material being added beyond this amount was far enough away from the thermocouple junction not to affect it appreciably. On this basis the effect of the degree of packing would be dependent upon the packing sensitivity of a material to varying applied pressures. Thus, care has to be taken to be sure that all of the added material is participating in a recorded reaction if quantitative work is being done on an overall weight basis. Nevertheless, these observations are encouraging because they suggest that the instrument can, with proper development, be used on a quantitative thermodynamic basis.

The sharpness and shape of a peak is determined by the rate of the reaction and the rate of heating. At slower rates the base of the peak is extended over a greater temperature range and the linear magnitude becomes less, although theoretically the enclosed area would remain constant for a given reaction.

However, the heat tends to equalize with the block and some decrease of the peak would probably be experienced for the slower reaction rates. With the method of recording the differential temperature against time an illusion of a sharp peak can be obtained with the faster heating rates by a shortening of the time axis.

All reactions dependent upon gaseous diffusion either out from or into the sample are logically sensitive to the packing density, heating rates, and atmospheric conditions. If the continuance of a reaction is dependent upon dissipation of a resultant gas or vapor, the ease of this dissipation would determine the degree of shift to higher temperatures. Such reactions as vaporization, decomposition, and reduction would be affected in this way. On the other hand, oxidation reactions would require the diffusion of oxygen into the sample. Any condition that would prevent such diffusion would cause a shifting of the reaction to higher temperatures.

Continuing slow reactions, because of slow diffusion rates of the reactants through their product, will not produce any significant deviations from the "zero" line of the differential temperature. Such reactions are difficult to study by D.T.A. methods.

Identification of Reactions

The differential thermal analysis, thus, shows the presence of heat effects at certain temperatures and provides some indication as to their magnitude and their rate. The identification is largely the result of logical and deductive interpretation of available information.

Weight loss determinations at corresponding temperatures would support suggestions of decomposition. This reaction could be further substantiated by use of other tools, such as x-ray diffraction, petrographic microscope, electron microscope. X-ray diffraction methods are probably most effective. On the other hand, oxidation reactions in some instances may show a gain of weight.

In other words stoichiometric calculations would correspond to weight changes experienced.

If an exothermic effect is thought to be due to crystallization, then x-ray diffraction patterns should show the presence of a new phase. However, any technique, chemical or otherwise, that would indicate participation of constituents in a reaction should be sufficient.

SUMMARY AND CONCLUSIONS

In summarizing, the ideal D.T.A. experimental unit would consist of a sample block with holes of a size to give both maximum sensitivity and resolving power, a continous constant rate heating source controlled proportionally without any appreciable reversals of the heating rate, and a recording potentiometer type of instrument, properly shielded from a.c. strays, for showing the differential temperature. The normal operating temperature is approximately 1100°C. but can be raised to 1500°C. with use of platinum or its alloys.

The D.T.A. method has been used extensively on a qualitative basis for identification of certain minerals and for study of reactions. Some quantitative studies have been reported on basis of weight percentages of certain minerals. Extensive work on quantitative thermal measurements is yet to be done.

It has excellent possibilities as a research tool in the study of reactions. Supplemental data, most difficult to obtain in other ways, becomes available for purposes of interpretation. The method also is easily adaptable as a control tool in the production of raw materials and at various steps in certain manufacturing processes. Small differences between samples are easily picked up.

ACKNOWLEDGMENTS

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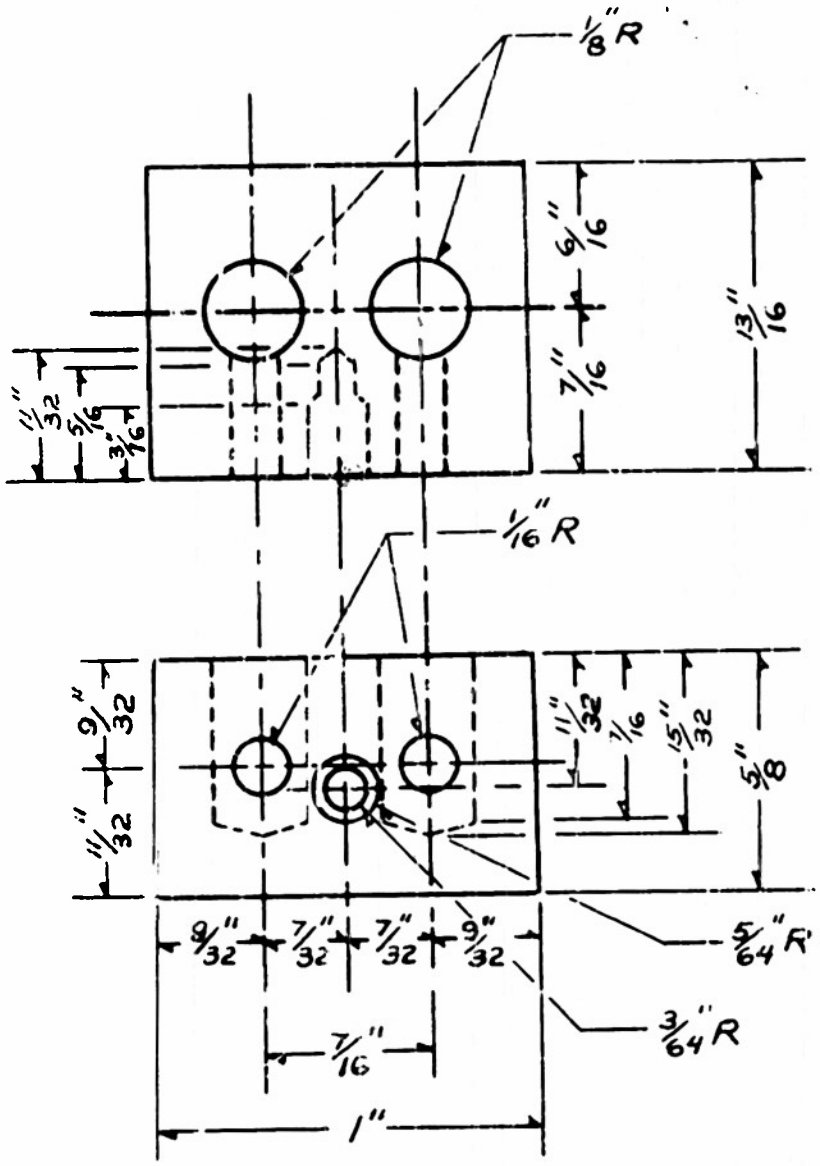
FIGURE 1. Sample Test Blocks

The drawing on the left represents a commonly used design. The one on the right is the design presently used in this laboratory.


1/8" R
1/16" R
9/16"
7/16"
13/16"
1/32"
5/16
3/16"
9/32"
11/32"
1/16
15/32"
5/8"
9/32"
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7/32"
9/32"
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3/64" R
7/16"
1"

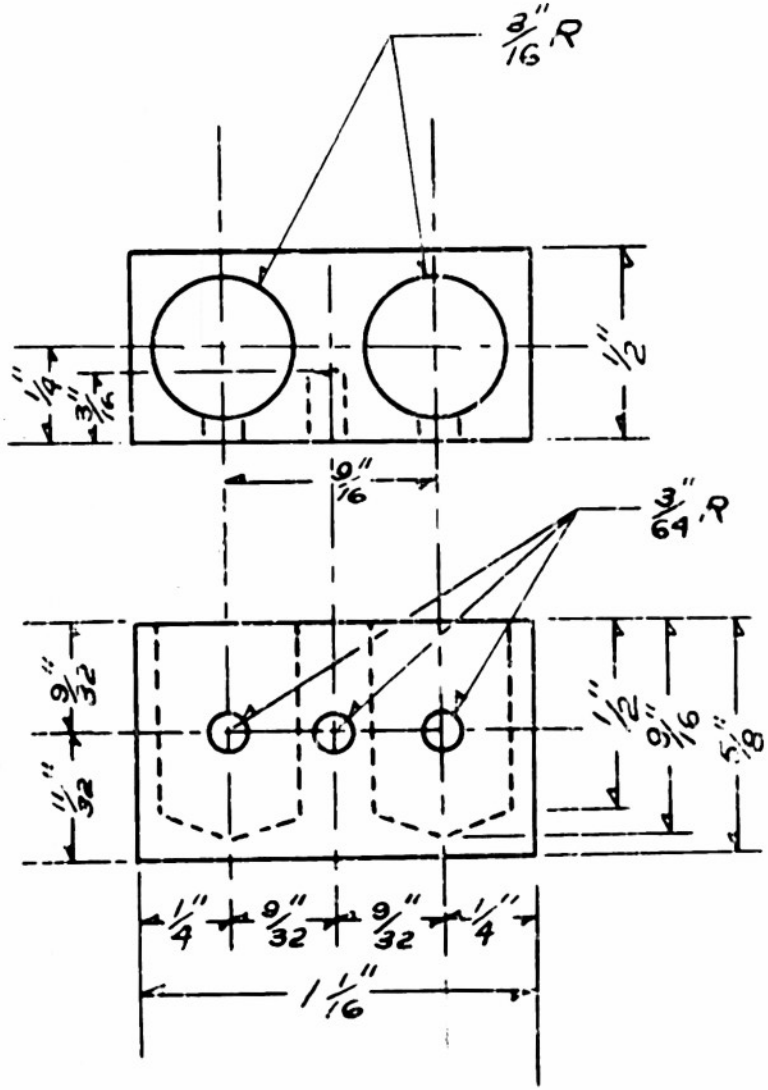
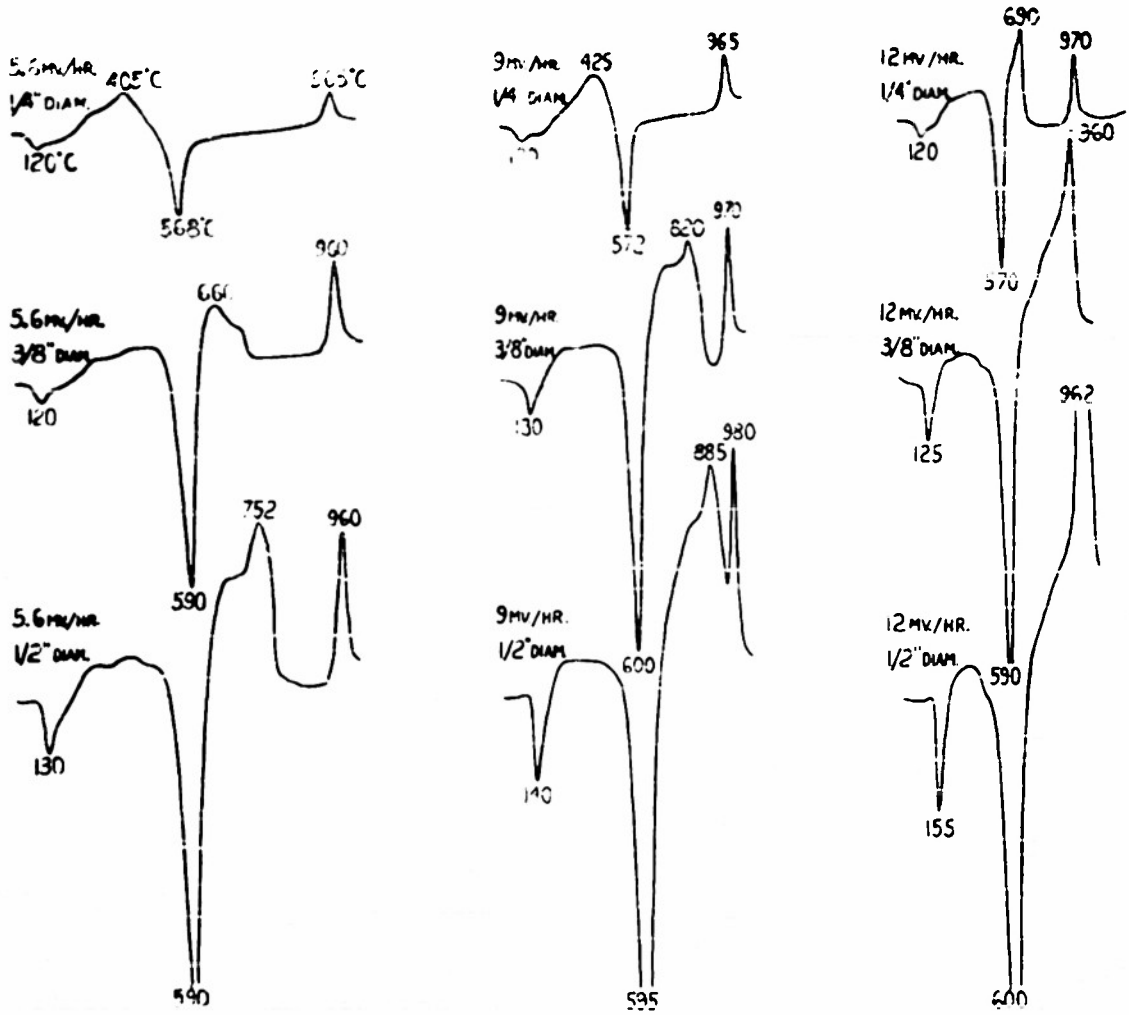

3/16" R
1/2"
1/4"
3/16"
9/16"
3/64" R
9/32"
11/32"
1/2"
9/16"
5/8"
1/4"
9/32"
9/32"
1/4"
1 1/16"

FIGURE 2. Differential Thermal Analysis Curves for a Ball Clay

In the upper set the resultant change in the shape of the curves is indicated by changing the volume of the sample by varying the diameter of the sample and reference holes ($\frac{1}{4}$, 3/8, and $\frac{1}{2}$") for three given heating rates of 5.6, 9, and 12 mv./hour using a platinum-10% rhodium thermocouple. The ratio of the overall bulk volume of the sample test block to the volume of the sample and reference holes was kept constant at 2.7 in this series.

The lower set of curves shows the changes resulting by changing the block-hole ratio (2.7, 5.8, and 10.6) for two sizes of hole diameters ($\frac{1}{4}$ and 3/8") at a constant heating rate of 9 mv./hour.

BLOCK BULK VOLUME/HOLE VOLUME = 2.7 (CONSTANT)



HEATING RATE = 9 MV.(Pt-10%Rh)/HR. (CONSTANT)

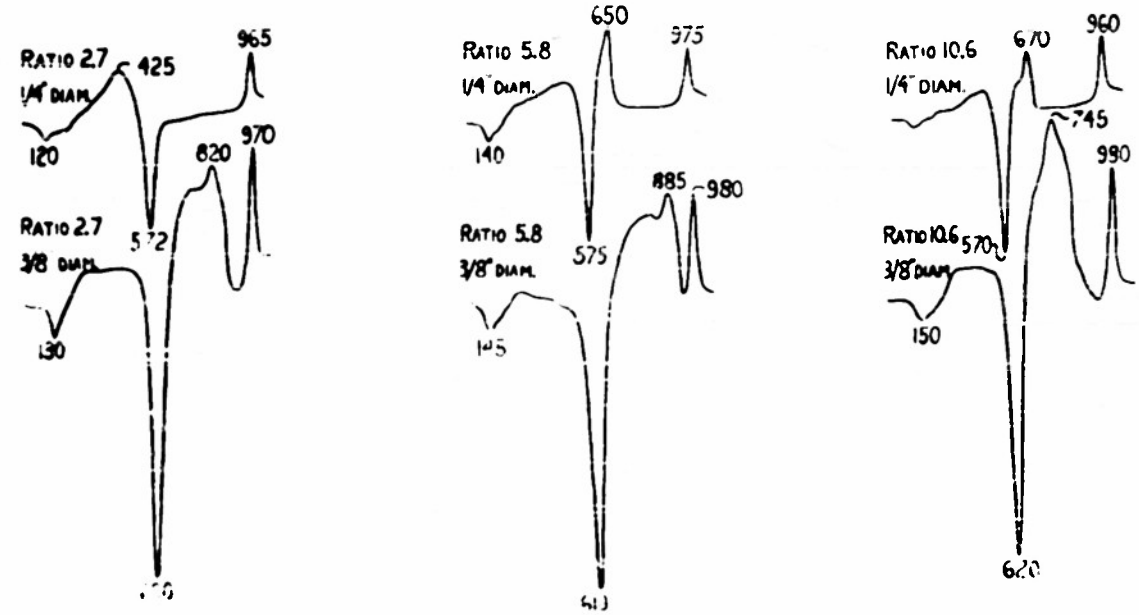
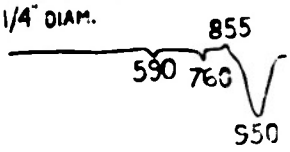


FIGURE 3. Differential Thermal Analysis Curves for Talc A

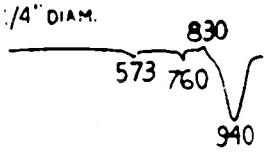
The curves show the changes resulting by varying the ratio of the overall bulk volume of the sample test block to the volume of the sample and reference holes (2.7, 5.8, and 10.6) for three different volumes of the sample as determined by diameter of the sample and reference holes ($\frac{1}{4}$, 3/8, and $\frac{1}{2}$"). The heating rate was constant at 9 mv./hour using a platinum-10% rhodium thermocouple.

HEATING RATE = 9 MV.(Pt-10%Rh)/HR.(CONSTAINT)

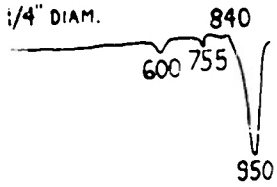
RATIO 2.7
1/4" DIAM.



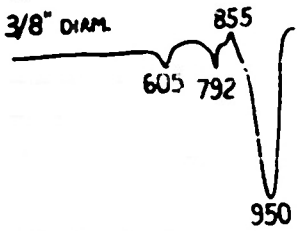
RATIO 5.8
1/4" DIAM.



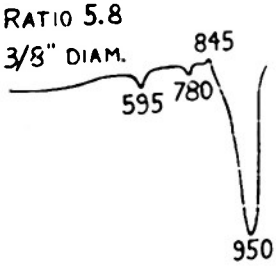
RATIO 10.6
1/4" DIAM.



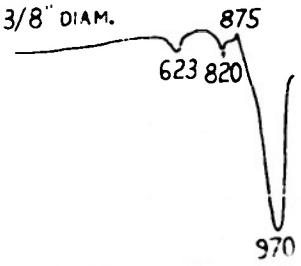
RATIO 2.7
3/8" DIAM.



RATIO 5.8
3/8" DIAM.



RATIO 10.6
3/8" DIAM.



RATIO 2.7
1/2" DIAM.

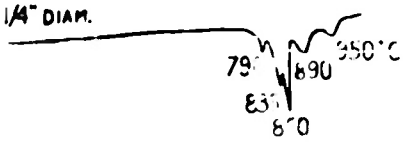
FIGURE 4. Differential Thermal Analysis Curves for Talc B

In the upper set the resultant change in the shape and resolving power of the curves is indicated by changing the volume of the sample by varying the diameter of the sample and reference holes ($\frac{1}{4}$, 3/8, and $\frac{1}{2}$") for three given heating rates of 5.6, 9, and 12 mv./hour using a platinum-10% rhodium thermocouple. The ratio of the overall bulk volume of the sample test block to the volume of the sample and reference holes was kept constant at 2.7 in this series.

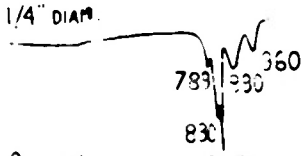
The lower set of curves shows the changes resulting by changing the block-hole ratio (2.7, 5.8, 10.6) for two sizes of hole diameters ($\frac{1}{4}$ and 3/8") at a constant heating rate of 9 mv./hour.

BLOCK BULK VOLUME/HOLE VOLUME = 2.7 (CONSTANT)

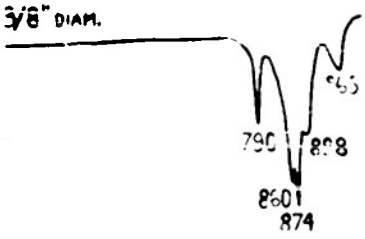
5.6 MV/HR.
1/4" DIAM.



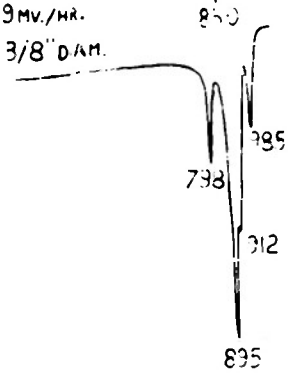
9 MV./HR.
1/4" DIAM.



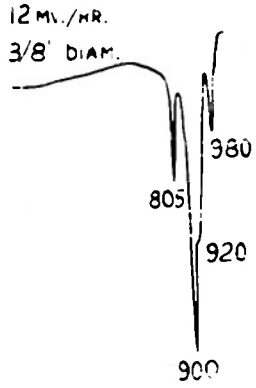
5.6 MV/HR.
3/8" DIAM.



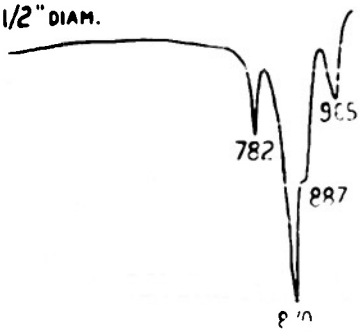
9 MV./HR.
3/8" DIAM.



12 MV./HR.
3/8" DIAM.

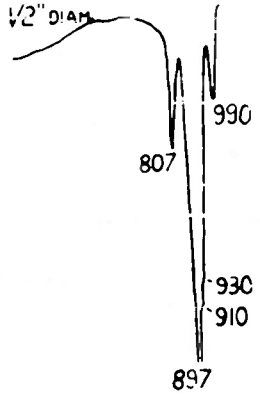


5.6 MV./HR.
1/2" DIAM.



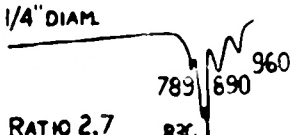
9 MV./HR.
1/2" DIAM.

12 MV./HR.
1/2" DIAM.

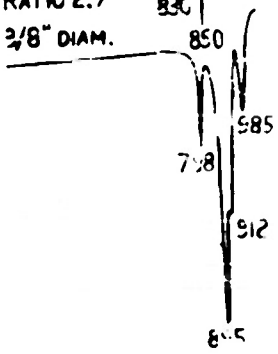


HEATING RATE = 9 MV. (Pt-10%Rh)/HR. (CONSTANT)

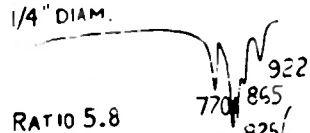
RATIO 2.7
1/4" DIAM.



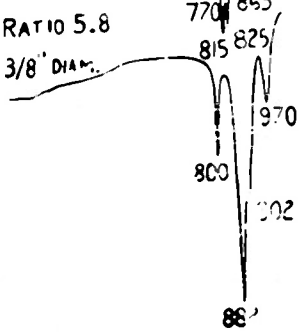
RATIO 2.7
3/8" DIAM.



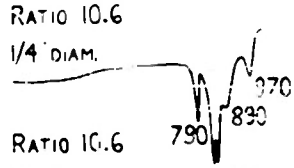
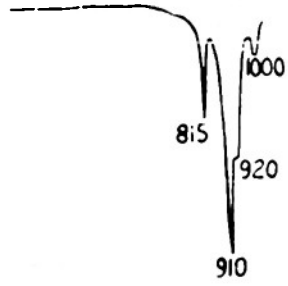
RATIO 5.8
1/4" DIAM.



RATIO 5.8
3/8" DIAM.



RATIO 10.6
1/4" DIAM.



RATIO 10.6
3/8" DIAM.